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Contract Nobs-90267
Project Serial No. SR001-03-01, Task 606

DEVELOPMENT OF NONFLAMMABLE HYDRAULIC FLUID

BUREAU OF SHIPS
Department of the Navy
Washington, D.C.

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DEVELOPMENT OF NONFLAMMABLE HYDRAULIC FLUID

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FOREWORD

This report was prepared by the Research and Development Department of the American Oil Company under U.S. Navy, Bureau of Ships Contract NObs-90267, Project Serial No. SR001-03-01, Task 606. Covered is work done from April 1, 1964 to June 1, 1964. The work was administered under the direction of the Chief, Bureau of Ships, Code 634A, with Mr. E. C. Davis as technical monitor.

ABSTRACT

The object of this study is the development of a water-base hydraulic fluid which (1) yields a fire-resistant non-aqueous residue, (2) is compatible with materials of construction and sea-water contamination, (3) satisfactorily lubricates shipboard pumps, (4) presents no unusual storage or handling problems, and (5) exhibits no toxicological hazards under conditions of use.

~~Considerable time~~ was spent on literature studies and on the ~~procurement~~ of supplies.

Five-pound batches of four commercial chemicals were purified by distillation.

Diethyl vinylphosphonate was synthesized and polymerized to yield a polymer of 1145 molecular weight.

Polyethylene grease (1800 molecular weight) was chlorophosphonated, hydrolyzed, and neutralized with sodium hydroxide to yield a water-soluble salt containing 15.5% phosphorus. Static tests showed a 10% solution of this product in water to be somewhat corrosive to steel and copper and non-corrosive to aluminum and galvanized steel.

DEVELOPMENT OF NONFLAMMABLE HYDRAULIC FLUID

INTRODUCTION

Two types of fire-resistant hydraulic fluids are being used in aircraft-carrier systems. The fluid used in hydraulic catapults is a mixture of water, glycol, polyglycols, and additives. An aromatic phosphate ester fluid is used in aircraft elevators. Because of the complexity of submarine hydraulic systems, both of these fluids have serious shortcomings. The water-glycol fluids are incompatible with sea water, are relatively poor lubricants for heavily loaded bearings, and are corrosive to aluminum. In addition, loss of water results in the formation of flammable residues. Because of fluid-leakage problems, phosphate esters cannot be used in submarines.

A satisfactory water base fluid for shipboard hydraulic-system use is needed. For the uses envisioned, fire resistance in both the finished fluid and the non-aqueous residue is of prime importance. In addition, the fluid must be capable of lubricating shipboard hydraulic pumps, be compatible with materials of construction and with 10% sea-water contamination, and present no unusual handling and storage problems. The fluid should be formulated to minimize toxicity hazards under conditions involving long periods of continuous exposure. Fluid residues should be removable by flushing with water.

In this study, the general approach consists of the synthesis and evaluation of water-soluble thickening agents which exhibit satisfactory fire-resistant properties. Development of thickening agents which allows formulation of a fluid having the desired fire-resistance, viscosity, and shear-stability characteristics will be followed by development of additives where necessary to impart satisfactory lubricating ability, oxidation and corrosion resistance, pourpoint, resistance to stable foam formation, and compatibility with sea water. When success, or near-success in the development of an appropriate thickening agent is indicated, it will be necessary to determine the toxicological hazards which may result from use of the fluid.

EXPERIMENTAL

The current program on nonflammable hydraulic fluids is aimed primarily at the development of a suitable water-soluble thickener which contains sufficient phosphorus to impart fire resistance to the non-aqueous residue.

Considerable time during the period reported herein was spent in literature studies, material procurement, and general preparations to begin the study. In addition, the following experimental work was carried out:

Distillation of Starting Materials

Approximately five pounds each of triethyl phosphite, 1,2-dibromoethane, 1-bromo-2-chloroethane, and allyl bromide were purified by distillation through a one-meter helix-packed column having 42 theoretical plates.

Diethyl Vinylphosphonate

Following the directions of Kosolapoff (JACS 70, 197 (1948)) diethyl vinylphosphonate was prepared in 46% yield by the reaction of triethyl phosphite and 1,2-bromoethane followed by dehydrohalogenation of the resulting diethyl 2-bromoethylphosphonate. In addition to the desired product, a considerable amount of higher-boiling material was obtained which gave a negative test with aqueous potassium permanganate for unsaturated linkages.

Polymerization of Diethyl Vinylphosphonate

Diethyl vinylphosphonate was polymerized at 135°C for sixteen hours using 0.1% t-butyl hydroperoxide as catalyst. Fifty percent conversion to a polymer of 1145 molecular weight was obtained.

Sodium Polyethylene Phosphinate

Polyethylene grease (molecular weight about 1800) was reacted with phosphorus trichloride and oxygen as described by Schroeder and Sopchak (J. Polymer Science 47, 417 (1960)). The product was poured into crushed ice and the hydrolyzed product was recovered by filtration. It was then dissolved in sodium hydroxide solution, filtered to remove a small amount of insoluble material, reprecipitated with dilute hydrochloric acid, and filtered. The sodium salt was then prepared by neutralization to pH 7 with aqueous sodium hydroxide and evaporation of water under vacuum. The resulting product was soluble in water and contained 15.5% phosphorus.

Static corrosion tests on a 10% solution of this salt in water were run on steel, copper, aluminum, and galvanized-steel strips. After three weeks, visual inspection indicated slight corrosion of the steel strip, very slight corrosion of the copper strip, and no corrosion of the aluminum and galvanized-steel strips.

FUTURE PROGRAM

Promising leads obtained to date will be followed. Methods for polymerization of diethyl vinylphosphonate to yield higher-molecular-weight polymers will be studied. Preparation of diethyl allylphosphonate has been started. Samples of polyethylenes of different molecular weight are being obtained and will be chlorophosphonated.